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Coal Fracturing Through Liquid Nitrogen Treatment: A Micro-Computed Tomography Study

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Abstract

Low permeability of coals has been a constant obstacle to economic production from coalbed methane reservoirs, and liquid nitrogen treatment has been investigated as one of the approaches to address this issue. This study thus examines cryogenic N_2 fracturing of a bituminous coal at pore scale through 3D X-ray micro-computed tomography. For this purpose, a cylindrical sample was immersed into liquid N_2 for 60 minutes. The micro-CT results obviously suggest that rapid freezing of the coal with liquid nitrogen generates fracture planes with large apertures rooting from the pre-existing cleats in the rock. This treatment also connected original cleats with originally isolated pores and micro-cleats, thereby increasing pore network connectivity. Moreover, SEM imaging highlighted the appearance of continuous wide conductive fractures with the maximum opening size of 9 µm. Furthermore, Nano-indentation technique was used to test the effect of liquid N2 on coal mechanical properties. The indentation moduli decreased by up to 14%, which was attributed to the increase in the cracked rock compressibility, thus considerable fracturing efficiency of the liquid N2 treatment. Therefore, through in-situ microscopic visualization and surface investigation, this study quantified the pore structure and connectivity evolution of the rock based on the

morphological alteration, and proved the promising effect of liquid N2 freezing on bituminous coals fracturing, aiding coalbed methane production.

1. Introduction

The significance of coal seams as a reliable source of energy is now manifest to the oil and gas industry. The global coalbed methane reserve has been estimated to exceed 8000 Tcf, and during the recent decades, the extraction of this source of energy has experienced an upward trend (Dong *et al.* 2012; Bahadori 2018). Production from these hydrocarbon resources is currently the intention of gas producing companies, although owing to the unique structure of coals, enhanced recovery is an inevitable stage in CBM exploitation.

Coals are fractured reservoirs in essence, and the cleat network plays the main role in the flow of fluids. The bulk of the gas is stored in matrix blocks, and the storage mechanism in coals is adsorption in such medium compared to compression in conventional reservoirs (Bedrikovetsky *et al.* 2012). Therefore, the permeability of a CBM is substantially affected by the permeability measure of cleat network (Seidle 2011). Accordingly, cleat permeability in coals has been vastly regarded to as the most influential factor in the production of the reservoir as well as economic evaluation of the field development (Shi and Durucan 2005; Connell *et al.* 2010; Pan *et al.* 2010; Pan and Connell 2012; Keshavarz *et al.* 2014; Keshavarz *et al.* 2016; Akhondzadeh *et al.* 2018).

However, owing to typical low Young's modulus of coals plus fracture mineralisation phenomenon, the permeability of coals is originally low, especially in deeper seams and higher rank coals (Rogers Rudy 2007). Furthermore, exclusive to coals, the permeability measure of coal reservoirs at any time in the production profile is a function of effective stress as a result of reservoir pressure drop, and matrix shrinkage as a result of gas desorption (Harpalani and

Chen 1995; Siriwardane *et al.* 2009). Therefore, techniques to increase the coal permeability have placed in the lime light of gas producers from coal seams.

Accordingly, in order to increase the chance of having a promising fluid flow rate in CBM exploitation, the fracture network is to be stimulated, being viable through inducing new fractures. This application has been implemented for decades through hydraulic fracturing (HF), which is basically injecting water to the reservoirs with pressures higher than the rock's breaking pressure. Although proved to be an efficient application, HF has its drawbacks in some cases, including technical or environmental obstacles, rendering some projects unsuccessful (Bahrami *et al.* 2012; Aguilera *et al.* 2014; Boudet *et al.* 2014). Li et al. (2015) suggested that although HF could result in a large-scale fracturing, clay swelling and huge water consumption would remain the issues (Li *et al.* 2016). In terms of environmentally friendly practices, due to generation of a large amount of contaminated water, application of this technology has been strictly banned by some states in the U.S. and a number of European countries (Nicot and Scanlon 2012; Middleton *et al.* 2015). The mentioned factors have drawn the attention of unconventional gas producers and researchers to anhydrous fracturing approaches such as using liquid nitrogen as the fracturing fluid (Cai *et al.* 2014b; Cha *et al.* 2014).

Liquid nitrogen (LN_2) injection has considerable benefits compared to injecting nitrogen in gaseous phase with the aim of fracturing the rock. LN_2 boiling point is at -196 °C at atmospheric pressure, and such vaporization generates the latent heat of 5.56 kJ/mol, that in turn result in an expansion of this gas to 696 times in the form of gas at 21 °C. Moreover, in water-bearing coals, the freezing of water provides another source of energy to fracture the rock (Qin *et al.* 2018). Therefore, the feasibility and efficiency of LN_2 fracturing has been the matter or research recently.

Reporting the results of five field applications, Mc.Danial et al. (1997) suggested that for formations with a medium depth, LN_2 fracturing using the thermal shock is possible, and such application does not damage the pipes, specially the casing. They put forward that the extent of shrinkage in coals plus their low thermal conductivity, generates fractures and micro-fractures with a perpendicular angle to the original fractures (McDaniel *et al.* 1997). Grundmann et al. (1998) injected liquid nitrogen into a shale reservoir, and reported that such approach is able to successfully increase the fractures via exceeding the rock's thermal tensile strength, although no adequate post-treatment flow results were reported (Grundmann *et al.* 1998).

Through subjecting three different types of rock, in dried and saturated states, to liquid nitrogen, Cai et al. (2014) suggested that pore structure is enhanced in general due to the thermal shock, and more importantly, the generated fractures make a considerable contribution to the effective porosity of the rock, because the micro-cracks branches from the pre-existing fractures (Cai *et al.* 2014b). Later in 2014, Cai et al. compared the fracturing capability of liquid nitrogen in a sandstone rock and a coal medium. They concluded that using liquid nitrogen as the hydraulic fracturing fluid is more promising in coals compared to sandstones. They also observed that when subjected to liquid nitrogen, the mechanical strength of the coal decreased, and the damage was positively correlated to water saturation. (Cai *et al.* 2014a)

Cai et al. (2015) submerged some dry coal samples in LN_2. While they observed surface cracks along the macro-fractures, the experiments revealed an increase of up to 34% and 93% in the compressive strength and permeability of treated samples, respectively (Cai *et al.* 2015). Conducting uniaxial compression tests and SEM, and investigating energy evaluation laws for dry coal samples treated with LN2, Cai et al. (2016) observed micro-fractures in the rock (Cai *et al.* 2016). A new fracturing process, taking advantage of in-situ liquid nitrogen gasification, was introduced by Li et al (Li *et al.* 2016).

Shi et al. (2017) examined LN_2 fracturing effect on mechanical properties alteration and pore structure evolution for several rocks. They observed that the Young's modulus and unconfined compressive strength of the coal samples reduced considerably, suggesting a considerable fracturing capability of liquid nitrogen in such medium (Shi *et al.* 2017). Qin et al. (2018) explored the potential of freeze-thaw cycling of LN_2 application in increasing the permeability and porosity of coals. They discussed that treating the rock with LN2 for one hour would generate fractures with the maximum aperture of 100 µm, and such long freezing duration contributes to a larger number of cross-linked-fractures, thereby increasing the apparent permeability (Qin *et al.* 2018).

While the mentioned studies have presented some noticeable information in LN_2 fracturing of rocks, the coal stimulation through such method yet requires better understanding to be practically encouraging. Therefore, any approach providing more detailed results would be a boon in this new research field, especially through 3D analysis.

Due to providing an illustrative 3-dimentional picture, Micro-Computed Tomography (micro-CT) has been relied on as a significant means of evaluating rocks in several processes, and has been used in coal studies as well (Iglauer and Lebedev 2017). Zhang et al. (2016) used micro-CT coupled with Scanning Electron Microscopy (SEM) in an attempt to explore the effect of water adsorption-related swelling of coal on the porosity and permeability reduction of the rock (Zhang *et al.* 2016). Zhang et al. (2017) investigated the fracturing mechanisms associated with supercritical CO_2 injection in a coal rock, using micro-CT and Nano-indentation experiments (Zhang *et al.* 2017). The effect of water adsorption on the mechanical properties alteration in coals was also investigated in a study by Zhang et al. (2018), in which micro-CT along with SEM and Nano-indentation tests were the means of evaluation (Zhang *et al.* 2018b). Micro-CT also benefitted a study aimed at characterizing the microstructure of a sub-bituminous coal applied by Zhang et al. (2018) (Zhang *et al.* 2018a). Karimpouli et al. (2017) combined micro-

CT images with a particular algorithm in order to more reliably reconstruct the heterogeneities and cleat network inside coal rocks (Karimpouli *et al.* 2017).

This paper is thus aimed at visualizing the morphological alteration of a bituminous coal rock in liquid nitrogen treatment through micro-CT imaging, and quantitatively analysing the data to measure the induced fractures and damages to the rock as the result of the treatment. The results of the micro-CT section would be then compared to scanning electron microscopy and Nano-indentation tests, to investigate the effect of this approach from different aspects, and verify the results.

2. Methodology

2.1 Coal sample preparation process

The rock used in this study was a bituminous coal buried in Morgantown, U.S., which was provided by Ward's Natural Science, USA, in the shape of chunk. The fixed carbon content of the coal is 88.7% and its volatile matter is 4.8%, and the mineral content composes of quartz, carbonate, clays and pyrite. The coal analysis was performed by Bureau Veritas - Minerals Pty Ltd, Australia. The coal block was drilled by a diamond coring bit with the internal diameter of 5 mm. The cylindrical sample was then polished on the both bases by 400 and 1200 grit sandpapers, sequentially. To provide a true cylindrical sample (in bases), we used a cuboid-shaped glass, and drilled a hole with the sample diameter, and put the coal sample inside the hole during polishing. The sample length following to the process was 10 mm. Such preparation of the sample guarantees reliable results in the experiments accomplished in this study. The process is illustrated in fig. 1.

2.2. Experimental procedure

To examine the fracturing potential of LN_2 on the rock, the coal was investigated through all the analysis before and after freezing. Preceding to start the tests, the prepared sample was vacuum dried at 60 ºC for 4 hours in an oven. The sample was then X-ray scanned with micro-computed tomography (Xradia Versa-XRM) at a resolution providing the voxel size of 1.37 μm^3.

Afterwards, the sample was scanned in a Hitachi SU3500 Scanning Electron Microscopy machine to acquire a base of comparison for post-treatment SEM images. The images, being from both the bases and the side of the cylindrical sample, were qualitatively compared, and for quantification purpose of the fractures' aperture size, ImageJ program was used. As the last pre-treatment test, the coal mechanical properties were examined at ambient condition (24 ºC) through an Ultra Micro Indentation System (UMIS), for which a Berkovich Nano-indenter was selected. The considered grid network (measure point array) was 4×4 in the Nano-indentation test with 200 μm spacing between each two adjacent indentation points, hence an area coverage of 0.8×0.8 mm^2. In this test, two tests with maximum forces of 10 mN and 35 mN were performed with 10 unloading points. The selected output of this test was Indentation modulus, the data of which was exported to IBM SPSS 25 statistics software for further data analysis. The Nano-indentation technique is described elaborately in (Zhang *et al.* 2018b). The sample was then submerged in liquid nitrogen for 60 minutes, whereas the treatment carried out in room temperature (24 ºC). A cryogenic container with the height of 40 cm was filled with LN_2 up to 30 cm, and obviously no noticeable change was observed in the height following the one hour. Subsequently the sample was tested through all the mentioned experiments to get the results the results for the treated rock.

2.3 Digital image analysis

The acquired 2D images through micro-CT tests were reconstructed to shape the 3D image of the scanned volume of the coal sample. The software used for image analysis was Thermo Scientific Amira-Avizo version 11.3.0. As the noise reduction technique, median filter with 3D interpretation was applied in the reconstructed volume. Median filter is a non-linear digital filtering method, which is considered to preserve the edges during noise reduction. Median filter is commonly applied as the pre-processing consideration for boosting the quality of image analysis methods such as segmentation and edge detection (Lore 2018). Subsequently, the watershed segmentation technique was applied to shape the four phases existing in the reconstructed images: exterior (the area around the sample cylinder), void space, organic matrix and mineral, in ascending order of colour intensity. Following to the segmentation, each of the defined phases consists of a number of different sized particles, based on which the quantitative data analysis is formed. It should also be mentioned that to have a better visualization on the segmented phases, a threshold (10^{-5} mm^3) was defined for the volume of all phases, below which no particles was shown. Please note that each particle is defined as one or a combination of voxels (pixel in 3D) that are surrounded by other phases, or in other words disjoint regions.

3. Results and discussion

3.1 Micro-Computed Tomography results

The segmentation process with watershed algorithm desirably distinguished the four defined phases in the 1.37 μm^3 voxel size micro-CT images of pre- and post-treatment with LN_2, as seen in Fig. 2 for a 2D cross section of the pre-treatment image.

Additionally, Fig. 3 illustrates a cross section of the original and treated digital rock. In order to conduct a reliable comparison, it was attempted to locate the same cross section in the reconstructed digital rocks of pre- and post-treatment images. Comparing the two top images (pre-treatment) with the below ones (post-treatment) in Fig. 3, reveals the promising efficiency of cryogenic liquid nitrogen to induce fracture in the treated rock. While the original rock did not contain any fractures with an opening larger than 10 µm was seen in the original rock, the largest fracture aperture size was observed to be 13 µm in the frozen sample. Additionally, another feature observed in this figure is that the induced fractures are interconnected to the pre-existing cleats, hence enhancing the apparent permeability of the rock, a phenomenon which would be further discussed in the 3D analysis section below.

The 3D analysis of the micro-CT images further reveals the efficiency of LN_2 fracturing. At first, the 3D images of the matrix phase in the rock in both before and after freezing states are to be discussed. The post-treatment image of the matrix phase of the digital rock highlights a new fracture, the extent of which is not clear on this image, as marked on Fig. 4. In order to visualize the extent of this fracture, the 3D phase of the pore distribution in the digital rocks should be evaluated.

Fig. 5 illustrates the volume of minerals and pore space for the original and the treated rock. Please note that the mentioned volume threshold filter (10^{-5} mm^3) is applied in this figure in order to get a better visualization on the cleat network and mineralization. These images prove the promising fracturing potential of liquid nitrogen approach through 3D analysis. While no noticeable fracture has appeared in the mineral phase after freezing, a considerable evolution is seen in the pore space of post-treatment. It is of a great importance to mention that the fracture marked I on the post-treatment images is not a totally newly-induced crack that has happened due to the treatment. This volume is made up of isolated pores and fractures that are now connected to the cleat network plus some new fractures. The reason it is being seen in this figure is that the interconnection of those volumes to the cleat network has pushed their volume size over the threshold, thus their appearance here. However, the fracture marked II in the post-treatment images of Fig. 5 is a totally new fracture, which is clearly rooted in the original cleats. Interestingly, this fracture is the one marked I in Fig.4. Therefore, not only LN2 fracturing induce new fractures, but also interconnects previously isolated pores and fractures with the original cleat network.

3.2 Scanning Electron Microscopy

Apart from the in-situ 3D morphological alteration analysis of the coal rock through micro-CT scan, the effect of cryogenic liquid nitrogen on the surface of the rock was also investigated. This investigation was performed at the bases and along the side of the sample, in pre-treatment and post-treatment states, as shown in Fig.6. Whereas no noticeable fracture is seen in the SEM images of the pre-treatment in the sample base and sides, the maximum fracture opening subsequent to the freezing was 9 µm, and fractures appeared in both bases and the sides, thus a new broad fracture network inside the whole rock, as verified by micro-CT results. Moreover, another critical feature of the post-treatment images is how the new fractures are thoroughgoing and generate a network, as seen in Fig. 6 (b). Therefore, SEM images are in consistency with the results of micro-CT, suggesting a considerable fracturing potential of this approach in bituminous coals.

3.3 Mechanical properties measurement through Nano-indentation

Mechanical properties examination of a fractured rock, could provide a further proof to the efficiency of the fracturing technique. Therefore, in this study, we used Nano-indentation to explore the damage occurs in a coal through liquid nitrogen fracturing. The results revealed that liquid nitrogen fracturing of the coal rock damages the rock inside.

Fig. 7 and Table 1 suggest that the indentation modulus (and in turn Young's modulus) of the coal though 10 mN and 35 mN indentation forces decreased by 5.1% and 14.4%, respectively. This reduction in the strength of the rock against an applied force is in line with the other findings of this study, because a fractured rock has a less strength and Young's modulus.

4. Conclusion

This study investigated the efficiency of liquid nitrogen fracturing of a bituminous coal through a 3D analysis. The over results are as follows:

Micro-CT results provide a visual understanding of the mechanism associated with liquid nitrogen fracturing. The 3D analysis suggests that not only this treatment generates new fractures in the rock (which are mostly rooted in the original fractures), but also interconnects the isolated pores and fractures with the original cleat network.

Moreover, the results of scanning electron microscopy provided evidence of the effect of liquid nitrogen fracturing on the surface of a coal rock. The images highlighted appearance of thoroughgoing fractures with the maximum opening size of 9 μm.

Finally, the mechanical properties analysis through Nano-indentation model verified the other findings of this study. The indentation modulus (which has a direct relationship with Young's modulus) decreased by up to 14.4%. Such considerable reduction reveals the existence of considerably extended new fractures inside the rock.

Conflicts of Interest

None.

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Biographies

Hamed completed his Bachelor’s and Master's in Petroleum Engineering. During his Master’s study, he conducted numerical research on heavy oil EOR. He used two of the most professional petroleum simulators, CMG and Eclipse, in his studies. He changed his research field to Coalbed Methane in 2016 and received a scholarship for his Ph.D. studies at Edith Cowan University (ECU), Australia. For the time being, as a Ph.D. student at ECU, he is experimentally researching on Coalbed Methane productivity enhancement as his priority, and also partially on enhanced oil recovery and CO_2 geo-sequestration. He is a member of SPE.

Alireza holds a Ph.D. degree in Petroleum Engineering from the University of Adelaide, an M.Sc. degree in Reservoir Engineering from the University of Tehran (Iran), and a B.Sc. degree in Chemical-Petroleum Engineering from Petroleum University of Technology (Iran). He is presently serving as a Senior Lecturer at the School of Engineering at Edith Cowan University. Before joining ECU, Alireza was a research scientist in the CSIRO-Energy business unit, where he researched enhancing gas production from unconventional resources and CO2-sequestration. Before pursuing his Ph.D. study, he was a Petroleum Engineer in the National Iranian Oil Company (NIOC) for six years. Alireza's research interests focus on Enhanced Oil/Gas Recovery from conventional and unconventional reservoirs. He is a member of SPE.

Faisal Ur Rahman Awan is an HDR Ph.D. candidate in Petroleum Engineering at Edith Cowan University, Australia. His work focuses specifically on the coal fines fixation using nanoparticles. Mr. Awan did his Bachelor's and Master's degrees in Petroleum Engineering. He has also been serving at Dawood University of Engineering and Technology, Karachi, as an Assistant Professor in Petroleum Engineering for the last seven years. He is a member of prestigious societies such as SPE, SEG, EI, and PEC.

Ahmed Yaseri is a Technical Support Officer at the School of Engineering for the Petroleum Engineering discipline. His research interests are in Rock Wettability, Formation damage, Multi phase flow in porous media, carbon dioxide storage and improved hydrocarbon recovery. Ahmed holds a PhD degree in Petroleum Engineering from Curtin University (Australia) and a MSc degree from Oklahoma University (USA). He is a member of SPE.

Stefan Iglauer joined Edith Cowan University (ECU) in 2018 as a Professor to lead the developments in the Petroleum Engineering discipline. His research interests are in petrophysics and interfacial phenomena, mainly at pore-scale with a focus on CO2 geo-sequestration and improved hydrocarbon recovery. Stefan has authored more than 250 technical publications; he holds a Ph.D. degree in material science from Oxford Brookes University (UK) and an MSc degree from the University of Paderborn (Germany). He is a member of SPE.

Maxim Lebedev did his Ph.D. in Physics from MIPT (Moscow Institute of Physics and Technology) USSR and B.S, M.S with High Distinction in Physics and Engineering. He has held several positions before joining Curtin University as Junior Researcher, Post-doctoral fellow, Senior Researcher, Research fellow and Principal engineer – Research at various research organisation. His research interest is in Experimental Rock Physics with focus on Rock Physics; Dynamic low strain core sample measurements; X-ray Computer Tomography; Ultrasonic measurements under stress. He is a member of SEG; ASEG; National Geographic Society.

References

Aguilera, R. F., Ripple, R. D., and Aguilera, R. (2014). Link between Endowments, Economics and Environment in Conventional and Unconventional Gas Reservoirs. *Fuel* **126**, 224-238.

Akhondzadeh, H., Keshavarz, A., Sayyafzadeh, M., and Kalantariasl, A. (2018). Investigating the Relative Impact of Key Reservoir Parameters on Performance of Coalbed Methane Reservoirs by an Efficient Statistical Approach. *Journal of Natural Gas Science and Engineering* **53**, 416-428.

Bahadori, A. (2018). 'Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs' (Gulf Professional Publishing.)

Bahrami, H., Rezaee, R., and Clennell, B. (2012). Water Blocking Damage in Hydraulically Fractured Tight Sand Gas Reservoirs: An Example from Perth Basin, Western Australia. *Journal of Petroleum Science and Engineering* **88**, 100-106.

Bedrikovetsky, P. G., Keshavarz, A., Khanna, A., Mckenzie, K. M., and Kotousov, A. Stimulation of Natural Cleats for Gas Production from Coal Beds by Graded Proppant Injection. In 'SPE Asia Pacific Oil and Gas Conference and Exhibition', 2012,

Boudet, H., Clarke, C., Bugden, D., Maibach, E., Roser-Renouf, C., and Leiserowitz, A. (2014). "Fracking" Controversy and Communication: Using National Survey Data to Understand Public Perceptions of Hydraulic Fracturing. *Energy Policy* **65**, 57-67.

Cai, C., Gao, F., Li, G., Huang, Z., and Hou, P. (2016). Evaluation of Coal Damage and Cracking Characteristics Due to Liquid Nitrogen Cooling on the Basis of the Energy Evolution Laws. *Journal of Natural Gas Science and Engineering* **29**, 30-36.

Cai, C., Li, G., Huang, Z., Shen, Z., and Tian, S. (2014a). Rock Pore Structure Damage Due to Freeze During Liquid Nitrogen Fracturing. *Arabian Journal for Science and Engineering* **39**(12), 9249-9257.

Cai, C., Li, G., Huang, Z., Shen, Z., Tian, S., and Wei, J. (2014b). Experimental Study of the Effect of Liquid Nitrogen Cooling on Rock Pore Structure. *Journal of Natural Gas Science and Engineering* **21**, 507-517.

Cai, C., Li, G., Huang, Z., Tian, S., Shen, Z., and Fu, X. (2015). Experiment of Coal Damage Due to Super-Cooling with Liquid Nitrogen. *Journal of Natural Gas Science and Engineering* **22**, 42-48.

Cha, M., Yin, X., Kneafsey, T., Johanson, B., Alqahtani, N., Miskimins, J., Patterson, T., and Wu, Y.-S. (2014). Cryogenic Fracturing for Reservoir Stimulation–Laboratory Studies. *Journal of Petroleum Science and Engineering* **124**, 436-450.

Connell, L. D., Lu, M., and Pan, Z. (2010). An Analytical Coal Permeability Model for Tri-Axial Strain and Stress Conditions. *International Journal of Coal Geology* **84**(2), 103-114.

Dong, Z., Holditch, S., McVay, D., and Ayers, W. B. (2012). Global Unconventional Gas Resource Assessment. *SPE Economics & Management* **4**(04), 222-234.

Grundmann, S. R., Rodvelt, G. D., Dials, G. A., and Allen, R. E. Cryogenic Nitrogen as a Hydraulic Fracturing Fluid in the Devonian Shale. In 'SPE Eastern Regional Meeting', 1998,

Harpalani, S., and Chen, G. (1995). Estimation of Changes in Fracture Porosity of Coal with Gas Emission. *Fuel* **74**(10), 1491-1498.

Iglauer, S., and Lebedev, M. (2017). High Pressure-Elevated Temperature X-Ray Micro-Computed Tomography for Subsurface Applications. *Advances in Colloid and Interface Science*.

Karimpouli, S., Tahmasebi, P., Ramandi, H. L., Mostaghimi, P., and Saadatfar, M. (2017). Stochastic Modeling of Coal Fracture Network by Direct Use of Micro-Computed Tomography Images. *International Journal of Coal Geology* **179**, 153-163.

Keshavarz, A., Badalyan, A., Carageorgos, T., Bedrikovetsky, P., and Johnson, R. (2014). Enhancement of Cbm Well Fracturing through Stimulation of Cleat Permeability by Ultra-Fine Particle Injection. *The APPEA Journal* **54**(1), 155-166.

Keshavarz, A., Badalyan, A., Johnson Jr, R., and Bedrikovetsky, P. (2016). Productivity Enhancement by Stimulation of Natural Fractures around a Hydraulic Fracture Using Micro-Sized Proppant Placement. *Journal of Natural Gas Science and Engineering* **33**, 1010-1024.

Li, Z., Xu, H., and Zhang, C. (2016). Liquid Nitrogen Gasification Fracturing Technology for Shale Gas Development. *Journal of Petroleum Science and Engineering* **138**, 253-256.

Lore, C. (2018). User's Guide-Avizo 9.5.

McDaniel, B., Grundmann, S. R., Kendrick, W. D., Wilson, D. R., and Jordan, S. W. Field Applications of Cryogenic Nitrogen as a Hydraulic Fracturing Fluid. In 'SPE annual technical conference and exhibition', 1997,

Middleton, R. S., Carey, J. W., Currier, R. P., Hyman, J. D., Kang, Q., Karra, S., Jiménez-Martínez, J., Porter, M. L., and Viswanathan, H. S. (2015). Shale Gas and Non-Aqueous Fracturing Fluids: Opportunities and Challenges for Supercritical Co 2. *Applied Energy* **147**, 500-509.

Nicot, J.-P., and Scanlon, B. R. (2012). Water Use for Shale-Gas Production in Texas, Us. *Environmental science & technology* **46**(6), 3580-3586.

Pan, Z., and Connell, L. D. (2012). Modelling Permeability for Coal Reservoirs: A Review of Analytical Models and Testing Data. *International Journal of Coal Geology* **92**, 1-44.

Pan, Z., Connell, L. D., and Camilleri, M. (2010). Laboratory Characterisation of Coal Reservoir Permeability for Primary and Enhanced Coalbed Methane Recovery. *International Journal of Coal Geology* **82**(3-4), 252-261.

Qin, L., Zhai, C., Xu, J., Liu, S., Zhong, C., and Yu, G. (2018). Evolution of the Pore Structure in Coal Subjected to Freeze− Thaw Using Liquid Nitrogen to Enhance Coalbed Methane Extraction. *Journal of Petroleum Science and Engineering*.

Rogers Rudy, E. (2007). Coalbed Methane: Principles and Practices. (Ed.^(Eds Editor.)(Mississippi: Oktibbeha Publishing Co. LLC.)

Seidle, J. (2011). 'Fundamentals of Coalbed Methane Reservoir Engineering' (PennWell Books.)

Shi, J.-Q., and Durucan, S. (2005). A Model for Changes in Coalbed Permeability During Primary and Enhanced Methane Recovery. *SPE Reservoir Evaluation & Engineering* **8**(04), 291-299.

Shi, X., Zhang, L., Cheng, Y., Li, B., and Yang, L. Pore Structure and Mechanical Property Change of Different Rocks under Nitrogen Freezing. In '51st US Rock Mechanics/Geomechanics Symposium', 2017,

Siriwardane, H. J., Gondle, R. K., and Smith, D. H. (2009). Shrinkage and Swelling of Coal Induced by Desorption and Sorption of Fluids: Theoretical Model and Interpretation of a Field Project. *International Journal of Coal Geology* **77**(1-2), 188-202.

Zhang, Y., Lebedev, M., Al-Yaseri, A., Yu, H., Xu, X., and Iglauer, S. (2018a). Characterization of Nanoscale Rockmechanical Properties and Microstructures of a Chinese Sub-Bituminous Coal. *Journal of Natural Gas Science and Engineering* **52**, 106-116.

Zhang, Y., Lebedev, M., Al-Yaseri, A., Yu, H., Xu, X., Sarmadivaleh, M., Barifcani, A., and Iglauer, S. (2018b). Nanoscale Rock Mechanical Property Changes in Heterogeneous Coal after Water Adsorption. *Fuel* **218**, 23-32.

Zhang, Y., Lebedev, M., Sarmadivaleh, M., Barifcani, A., Rahman, T., and Iglauer, S. (2016). Swelling Effect on Coal Micro Structure and Associated Permeability Reduction. *Fuel* **182**, 568-576.

Zhang, Y., Zhang, Z., Sarmadivaleh, M., Lebedev, M., Barifcani, A., Yu, H., and Iglauer, S. (2017). Micro-Scale Fracturing Mechanisms in Coal Induced by Adsorption of Supercritical Co2. *International Journal of Coal Geology* **175**, 40-50.

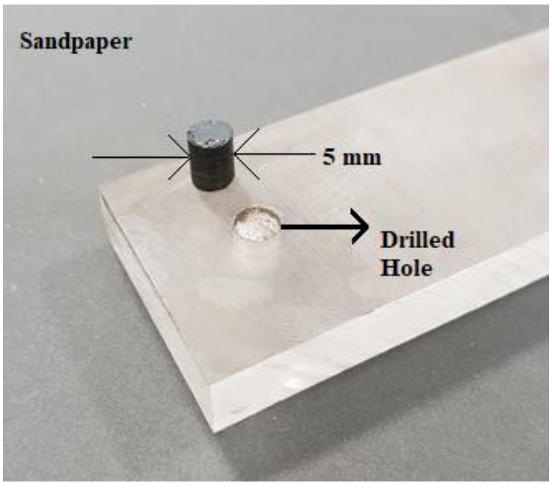

Fig. 1. Polishing process and the coal sample

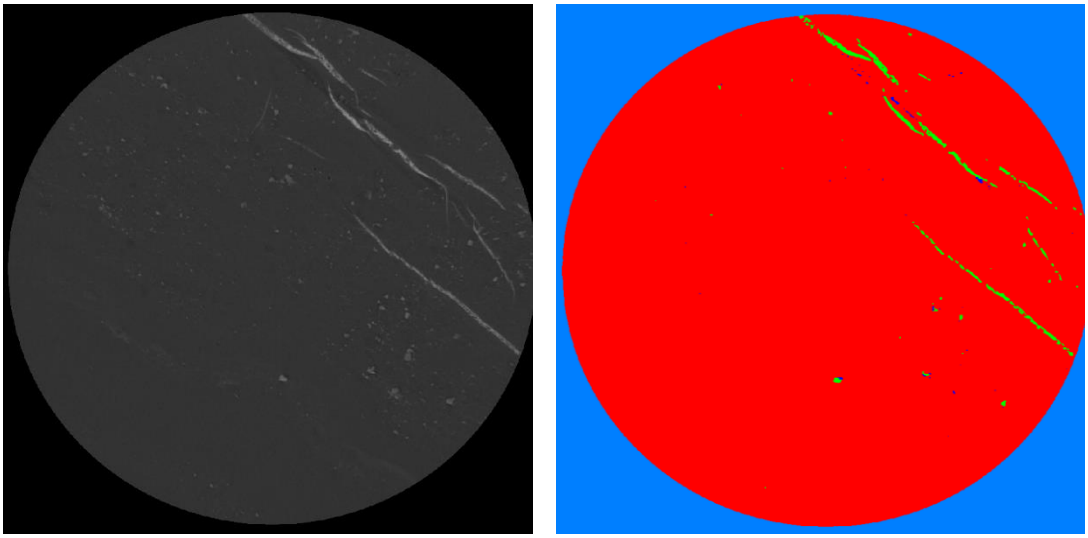

Fig. 2. Watershed segmentation of a 2D slice in the pre-treated rock: raw image (left) and segmented image (right). Light blue: exterior (the area around the rock), dark blue: pore, red: matrix and yellow: minerals.

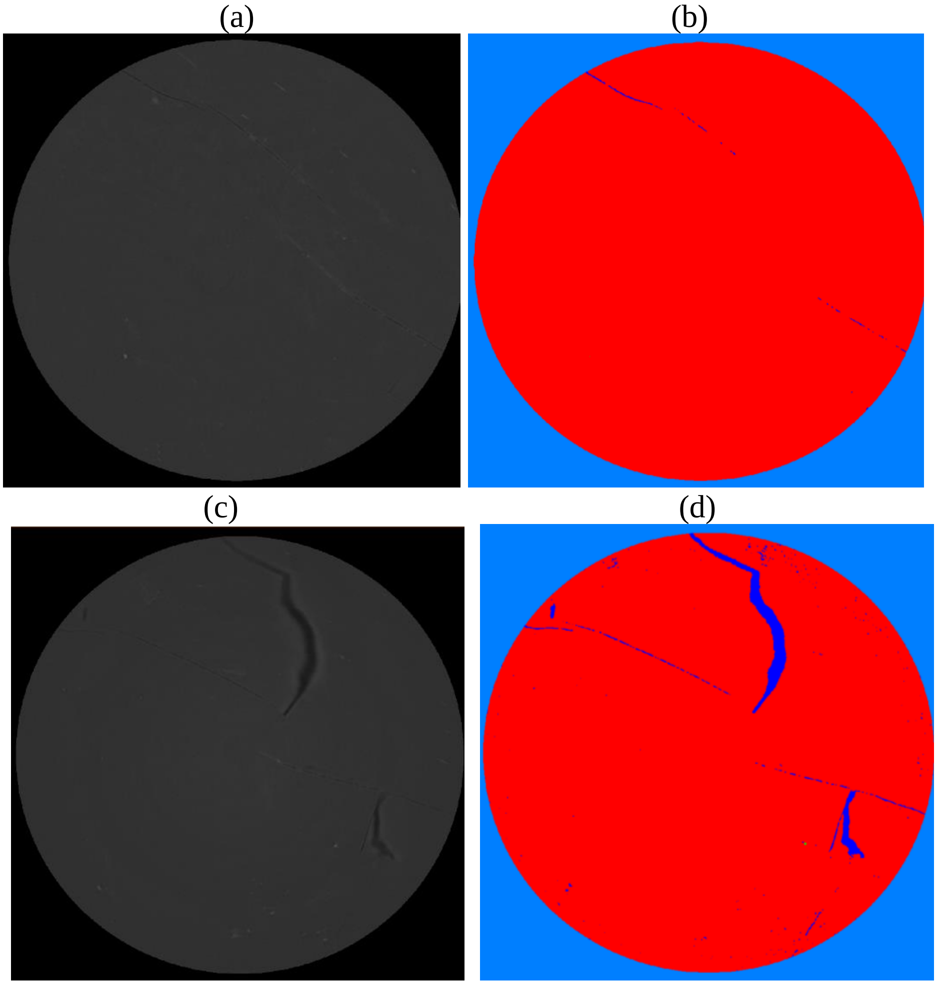

Fig. 3. A selected 2D slice of the rock: pre-treated raw (a) pre-treated segmented (b) post-treated raw (c) and post-treatment treated (d). Light blue: exterior, dark blue: pore, red: matrix and yellow: minerals.

Fig. 4. Organic matrix phase of the coal before (left) and after treatment

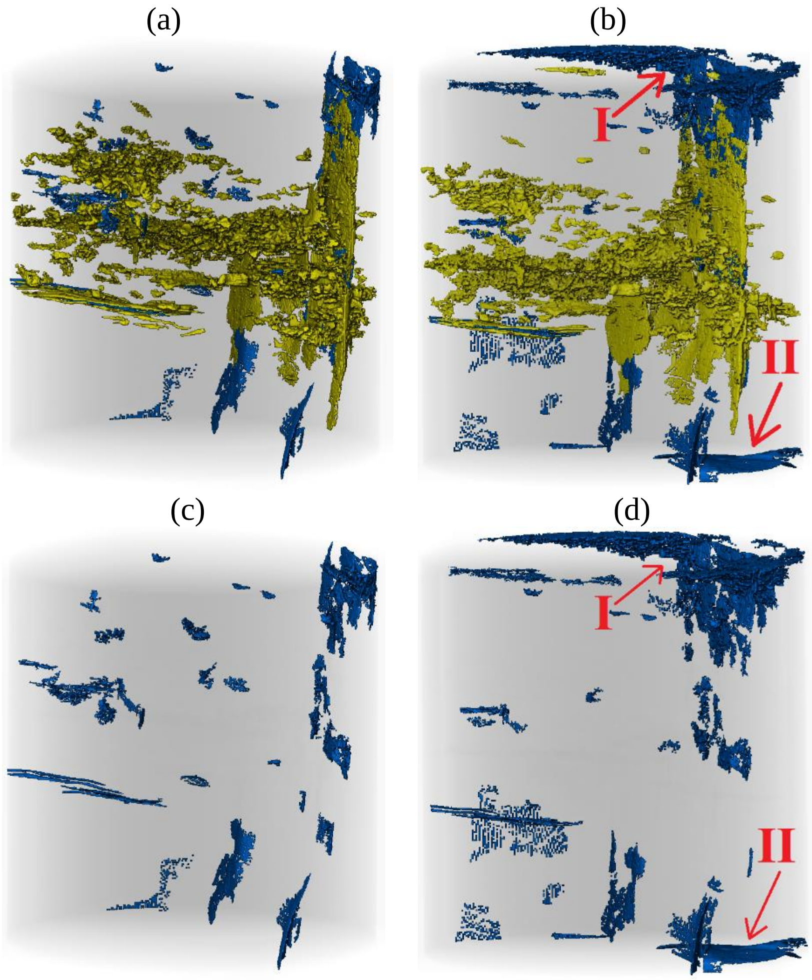

Fig. 5. Mineral and pore volume illustration of the digital rocks: pre-treatment (left) and post-treatment (right). Blue: void space and yellow: mineral phase.

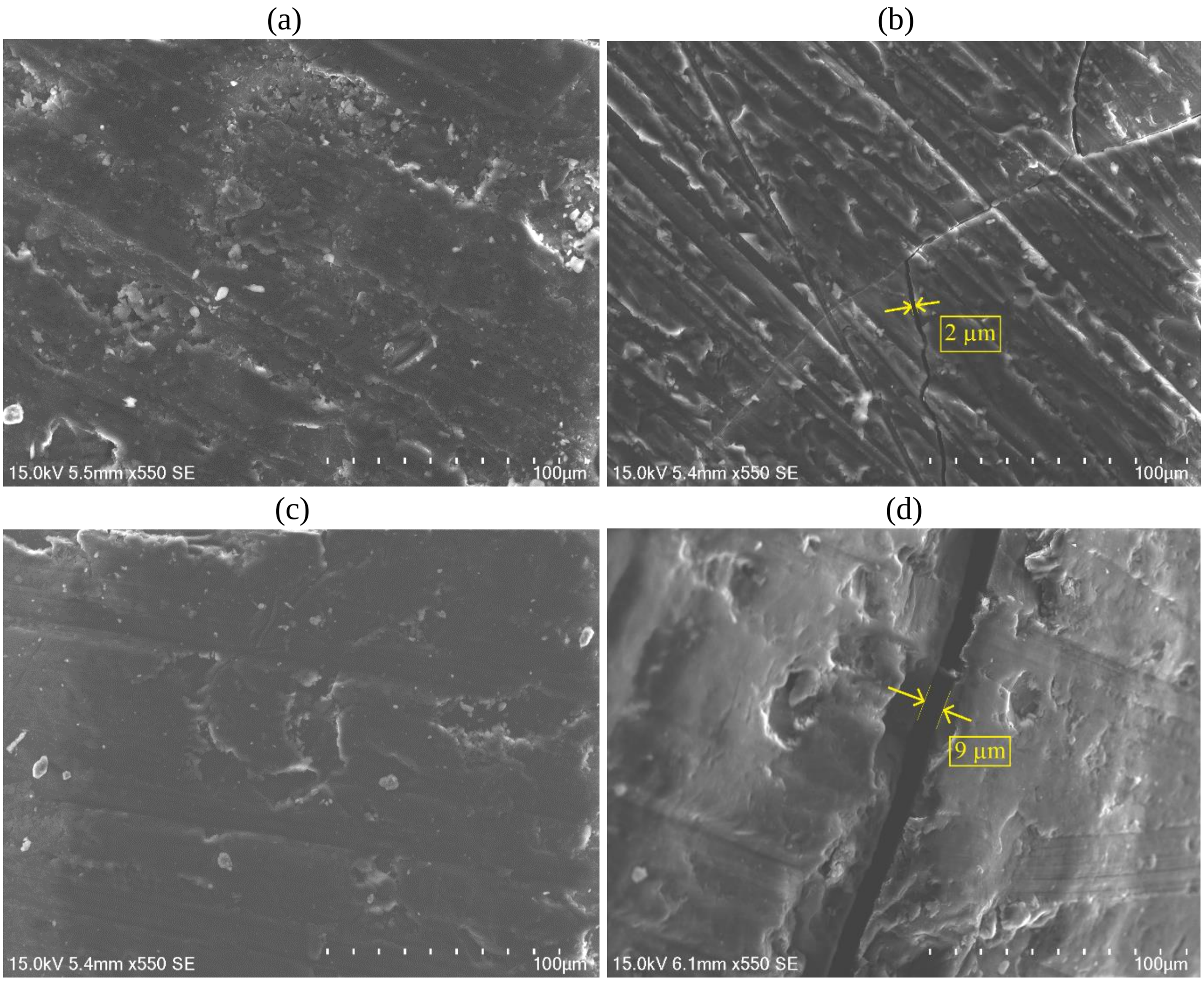

Fig. 6. SEM images of the coal sample: before freezing base (a) after freezing base (b) before freezing sides (c) and after freezing sides (d)

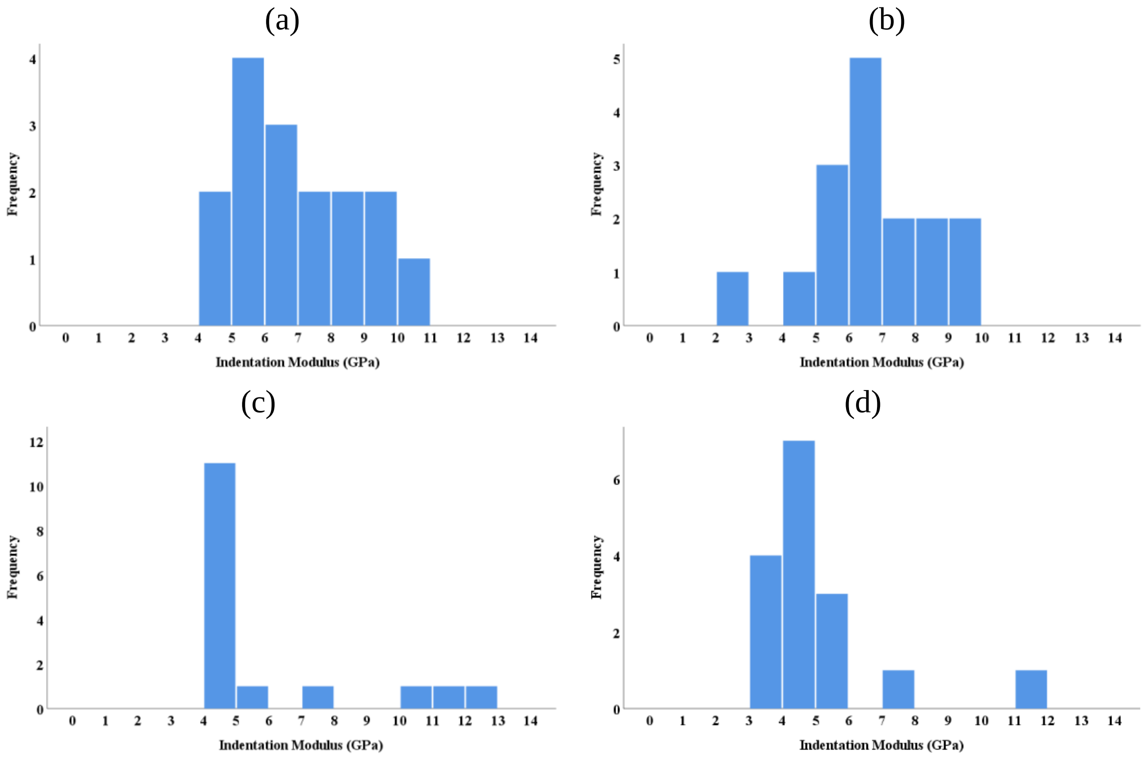

Fig. 7. Mechanical properties measurement by Nano-indentation technique: 10 mN pre-treatment (a) 10 mN post-treatment (b) 35 mN pre-treatment (c) 35 mN post-treatment (d)

Table 1. The summarized results of the Nano-indentation tests

	Mean indentation modulus (Gpa)		Indentation modulus reduction rate
Intentation Force	Original rock	Treated rock	
10 mN	7.04	6.68	5.1%
35 mN	5.98	5.12	14.4%